

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 5-12-95		3. REPORT TYPE AND DATES COVERED Final 4-1-87 to 9-30-89	
4. TITLE AND SUBTITLE Activation of Carbon Dioxide by Formation of Metalloheterocycles and Metallocycles				5. FUNDING NUMBERS Grant: N00014-87-K-0228 R&T: 413j007	
6. AUTHOR(S) N. John Cooper					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of Pittsburgh Pittsburgh, PA 15260				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of the Chief of Naval Research Arlington, VA 22217-5000				10. SPONSORING/MONITORING AGENCY REPORT NUMBER  DTIC QUALITY INSPECTED 5 JUL 14 1995 F	
11. SUPPLEMENTARY NOTES -					
12a. DISTRIBUTION/AVAILABILITY STATEMENT This document has been approved for public release and sale; its distribution is unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  The objective of this project was to find new ways to incorporate carbon dioxide into organic molecules by activation of the carbon dioxide within the coordination sphere of an electron rich transition metal complex. Achievements included the discovery that heteroallenes characteristically undergo reductive disproportionation with dianionic carbonylmetals and can add to electron rich neutral carbonyl complexes such as $[W(\eta^5-C_5H_5)_2(CO)]$ to give metalloheterocycles. We have further observed that unsaturated ligands can be induced to couple with carbon dioxide by reducing the metal center so that it will activate the carbon dioxide, as exemplified by bis-carboxylation of the carbene or carbenoid ligand in the two electron reduction products of Fischer carbene complexes with phosphine substituents to give substituted malonates, and by endo carboxylation of the $\eta^4$ -arene in the Cr(-II) complex $[Cr(\eta^4-C_6H_6)(CO)_3]^{2-}$ . We have also prepared $K[Co(2,6-C_6H_3NC)_4]$ , the first example of a homoleptic isonitrile complex of a metal in a negative oxidation state and the antecedent for a new class of transition metal complexes.					
14. SUBJECT TERMS carbon dioxide/heteroallene/transition metal/metalloheterocycle				15. NUMBER OF PAGES 7	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT		

# OFFICE OF NAVAL RESEARCH

GRANT# N00014-87-K-0228

R&T Code 413j007

Program Officer: Dr. Harold E. Guard

## FINAL REPORT

### Activation of Carbon Dioxide by Formation of Metalloheterocycles and Metallocycles

N. John Cooper

Chemistry Department, University of Pittsburgh

Pittsburgh, PA 15260

Submitted May 12, 1995

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale: its distribution is unlimited.

19950710 123

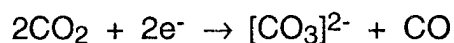
## Objective and Approach

The primary objective of this project was to find new ways to incorporate carbon dioxide into organic molecules by activation of the carbon dioxide within the coordination sphere of a transition metal complex.

Our experiments involved three inter-related approaches: the preparation of new classes of organometallic molecules designed to react with carbon dioxide and to couple carbon dioxide with unsaturated ligands within the coordination sphere of the metal; investigation of the reactions of carbon dioxide with such complexes; investigations of similar reactions of heteroallenes in cases in which the heteroallene reaction would provide additional insight into the carbon dioxide reactions.

## Results and Conclusions

Our experiments were guided by our previous ONR sponsored research on our discovery that highly electron rich dianionic carbonylmetalates  $[M(CO)_5]^{2-}$  ( $M = Cr, Mo, W$ ) and  $[M(CO)_4]^{2-}$  ( $M = Fe, Ru, Os$ ) form  $CO_2$  complexes in which the  $CO_2$  is activated because the ligand is bonded to the metal through carbon. This dramatically increases the nucleophilicity of the oxygen atoms, such that the adducts react readily with additional  $CO_2$  to form carbonate ion and coordinated CO in a sequence which constitutes an overall reductive disproportionation of  $CO_2$ :



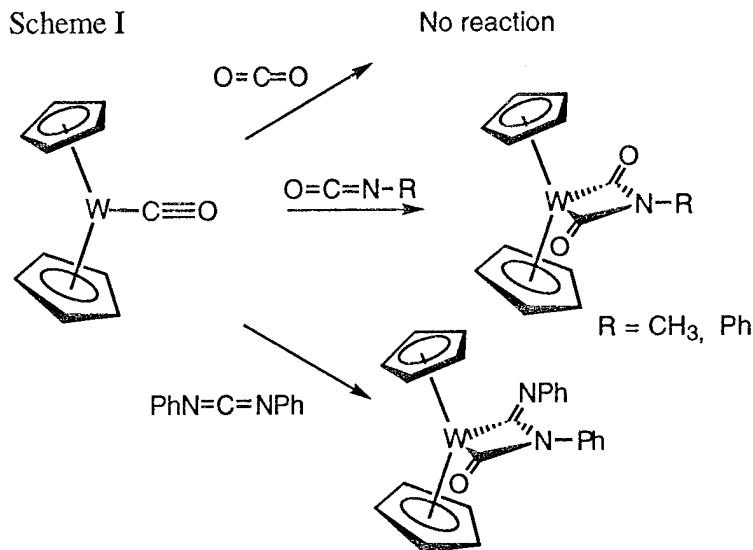
Carbon dioxide is the archetypal example of a heteroallene ( $X=C=Y$ ), and in this grant cycle we were able to establish that activation by coordination to a dianionic metal center is a general reaction of heteroallenes with dianionic carbonylmetalates. If one end of the heteroallene is capped by a first row element (N or O) which can form a strong triple bond with C, addition of a second equivalent of the heteroallene results in  $X^{2-}$  transfer to the second heteroallene molecule to give a heterocarbonate ion and leave a coordinated "heterocarbonyl". The net effect is that the dianionic carbonylmetalates induce reductive disproportionation of the heteroallene, and examples we have observed include the reactions of carbodiimides, carbonyl sulfide, isocyanates and thioisocyanates shown in Table I and reported in detail in Technical Report 1 and Publication 2.

Table I

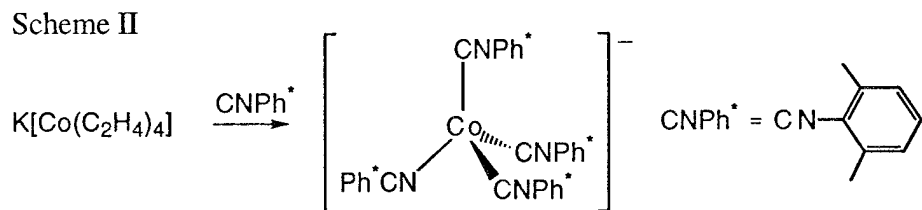
heteroallene	carbonylmetalate	initial product (solution yield)	isolated product/derivative (%)
COS	$Na_2[Fe(CO)_4]$	$[Fe(CO)_5]$ (73)	$[Fe(CO)_4I_2]$ (72)
COS	$Na_2[Ru(CO)_4]$	$[Ru(CO)_5]$	$[Ru(CO)_4I_2]$ (72)
COS	$Na_2[Cr(CO)_5]$	$[Cr(CO)_6]$	$NBu_4[Cr(CO)_5Br]$ (82)
COS	$Na_2[W(CO)_5]$	$[W(CO)_6]$ (74)	$NBu_4[W(CO)_5Br]$ (57)
COS	$Na_2[W(CO)_5]$	$[W(CO)_6]$	$[W(CO)_6]$ (61)
PhNCS	$Na_2[Fe(CO)_4]$	-	$[Fe(CO)_4(CNPh)]$ (42)
MeNCS	$Na_2[Fe(CO)_4]$	$[Fe(CO)_5]$	$[Fe(CO)_4(CNCH_3)]$ (24)
PhNCS	$Li_2[Cr(CO)_5]$	-	-
PhNCO	$Na_2[W(CO)_5]$	$[W(CO)_6]$ (84) + $[W(CO)_5(CNPh)]$ (5)	-
PhNCNPh	$Na_2[Fe(CO)_4]$		$[Fe(CO)_4(CNPh)]$ (10)

The observation in this work most directly relevant to our primary focus on CO<sub>2</sub> chemistry is that the direction of reductive disproportionation of asymmetric heteroallenes is controlled by the relative C≡X triple bond strengths in the reduced products (C≡O > C≡N > C≡S).

We have explored the activation of CO<sub>2</sub> and other heteroallenes by carbonyl complexes which are electron rich but not anionic, and we have observed, for example, that although [W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)] does not react with CO<sub>2</sub>, heteroallenes do add to the electron rich metal center to give metalloheterocycles (as illustrated for two cases in Scheme I) in which the heteroallene has been activated by coordination to the metal center in such a way that one of the heteroatoms adds to the carbon of the carbonyl ligand (Technical Report 2 and Publication 3).



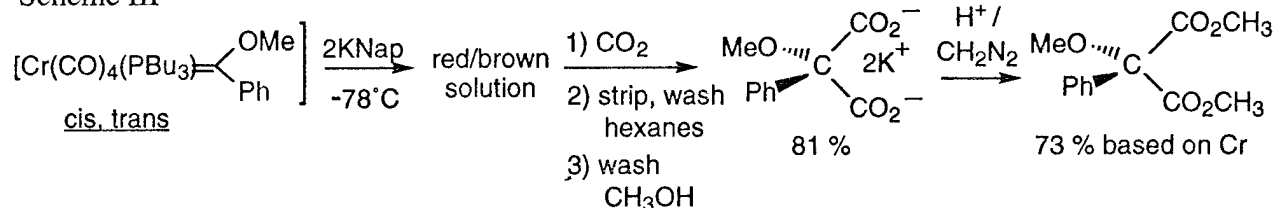
We have sought to prepare new classes of highly reduced transition metal complexes with the potential to activate CO<sub>2</sub>, and we targeted in particular systems containing longitudinally unsaturated ligands with the potential to couple to coordinated CO<sub>2</sub> ligands. This led us to prepare an isonitrile complex of Co(-I) by addition of an aryl isonitrile to the highly reduced alkene complex K[Co(C<sub>2</sub>H<sub>4</sub>)<sub>4</sub>] to displace the ethylene ligands and give K[Co(2,6-C<sub>6</sub>H<sub>3</sub>NC)<sub>4</sub>] as described in Technical Report 3 and Publication 4. This anion does not undergo coupling reactions when treated with CO<sub>2</sub>, but it is the first reported example of a homoleptic isonitrile complex of a metal in a negative oxidation state. We have termed such species isonitrilates, and it seems probable that K[Co(2,6-C<sub>6</sub>H<sub>3</sub>NC)<sub>4</sub>] is only the first example of a large class of new transition metal complexes.



We have observed that the unsaturation between the metal center and the carbenoid carbon in transition metal carbene complexes can be used to couple the carbene fragment with CO<sub>2</sub> if the metal is reduced to activate it with respect to addition of the electrophilic CO<sub>2</sub>. This was done as described in Technical Report 6 and Publication 6 by 2-electron naphthalenide reduction of Fischer

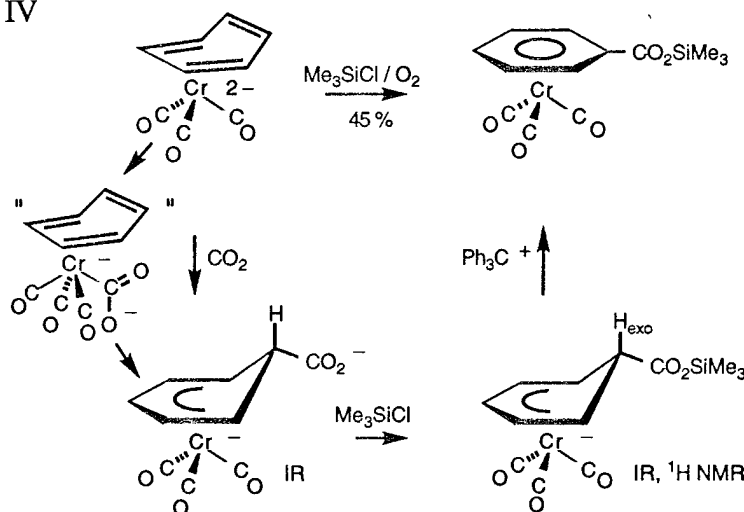
carbene complexes of Cr with phosphine substituents on the metal center (Scheme III), and although the nature of the reduced species has not been established we have shown that the carbene or carbenoid ligand will react readily with CO<sub>2</sub> in unprecedented bis-carboxylation reactions which give a previously unreported malonate with both aryl and methoxy substituents:

Scheme III



The key to this sequence is the combination in a single complex of the basic highly reduced metal center which can coordinate and activate the CO<sub>2</sub> with the unsaturation required for a coupling reaction. We have shown that this combination can be achieved in other ways by determining that the  $\eta^4$ -arene in the Cr(-II) complex [Cr( $\eta^4$ -C<sub>6</sub>H<sub>6</sub>)(CO)<sub>3</sub>]<sup>2-</sup> can be carboxylated with endo stereochemistry (demonstrating that the reaction is metal mediated) as shown in Scheme IV and described in Technical Report 5 and Publication 5.

Scheme IV



Much of our ONR sponsored research involves reactions of exceptionally air sensitive (particularly O<sub>2</sub> sensitive) molecules. There are many techniques for the manipulation of such materials under inert atmospheres, but it is often particularly convenient to handle them in solution by using differential pressures of an inert gas to transfer solutions between vessels through steel or Teflon cannulae. We are recognized as skilled and innovative practitioners of such techniques, and we were invited to participate in a tutorial at an ACS national meeting on the handling of air sensitive materials and to contribute a lead section in the successful 1987 book based on this tutorial. This chapter (Publication 1) was circulated as Technical Report 4.

The six publications supported by this grant have been in the literature for an average of 6 years, which provides an opportunity to assess their impact as indicated by how often they have been cited by other scientists. A search in Science Citation Index has established that they have been cited a total of 70 times to date.

## ONR Supported Graduate Students

Samkeun Lee  
Joseph A. Corella II  
Kuo-chen Shih  
Sherri R. Lovelace

## ONR Supported Postdoctoral Associate

Dr. Garry F. Warnock

## Highlighted Presentations

Our ONR sponsored research on the transition metal chemistry of carbon dioxide continues to attract considerable attention despite the drastic reduction in our efforts following the completion of this grant, and I was invited to present some of our results in a symposium on Small Molecule Activation at the 30th International Conference on Coordination Chemistry in Kyoto, Japan, in 1994. This biennial conference is the most important international conference devoted to coordination chemistry, and my talk centered on the carboxylation of highly reduced carbene complexes described in Technical Report 6 and Publication 6.

At a complementary level, a more general talk which discusses the transition metal chemistry of CO<sub>2</sub> within the context of the greenhouse effect and global warming continues to be the most requested and popular of the talks which I give when visiting small colleges to recruit prospective graduate students.

## Publications supported by ONR grant N00014-87-K-0228

### A. Book Chapters:

- (1) Cannula techniques for the manipulation of air sensitive materials. J. P. McNally, V. S. Leong and N. J. Cooper, "Experimental Organometallic Chemistry, A Practicum in Synthesis and Characterization", A. L. Wayda and M. Y. Darensbourg, Ed.; American Chemical Society: Washington, 1987; Chapter 2.

### B. Published papers in refereed journals:

- (2) Reactions of dianionic carbonylmetalates with heteroallenes: reduction of carbonyl sulfide, isothiocyanates, isocyanates and carbodiimides by group 6 and 8 carbonylmetalates. G. R. Lee and N. J. Cooper, *Organometallics*, 1989, 8, 1538.
- (3) Formation of metalloheterocycles by addition of heteroallenes to the electron-rich carbonyl complex [W( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)]. P. Jernakoff and N. J. Cooper, *J. Am. Chem. Soc.*, 1989, 111, 7424.
- (4) The first transition metal isonitrilate: synthesis and characterization of K[Co(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC)<sub>4</sub>]. G. F. Warnock and N. J. Cooper, *Organometallics*, 1989, 8, 1826.

- (5) Metal mediated addition of carbon dioxide to the activated benzene in  $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$ . J. A. Corella II and N. J. Cooper, J. Am. Chem. Soc., 1990, 112, 2832.
- (6) Highly reduced carbene complexes: formation of an alkoxymalonate by coupling of carbon dioxide with the nucleophilic carbene in  $[\text{Cr}(\text{CO})_4\{\text{=C}(\text{OMe})\text{Ph}\}]^{2-}$ . S. Lee and N. J. Cooper, J. Am. Chem. Soc., 1990, 112, 9419.

### Technical Reports supported by ONR grant N00014-87-K-0228

Technical Report No 1, submitted 7-15-88:

Reactions of dianionic carbonylmetalates with heteroallenes: reduction of carbonyl sulfide, isothiocyanates, isocyanates and carbodiimides by group 6 and 8 carbonylmetalates. G. R. Lee and N. J. Cooper

Technical Report No 2, submitted 1-5-89:

Formation of metallocycles by addition of heteroallenes to the electron-rich carbonyl complex  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ . P. Jernakoff and N. J. Cooper

Technical Report No 3, submitted 1-5-89:

The first transition metal isonitrilate: synthesis and characterization of  $\text{K}[\text{Co}(\text{2,6-Me}_2\text{C}_6\text{H}_3\text{NC})_4]$ . G. F. Warnock and N. J. Cooper

Technical Report No 4, submitted 7-31-89:

Cannula techniques for the manipulation of air sensitive materials. J. P. McNally, V. S. Leong and N. J. Cooper

Technical Report No 5, submitted 7-31-89:

Metal mediated addition of carbon dioxide to the activated benzene in  $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$ . J. A. Corella II and N. J. Cooper

Technical Report No 6, submitted 11-17-89:

Highly reduced carbene complexes: formation of an alkoxymalonate by coupling of carbon dioxide with the nucleophilic carbene in  $[\text{Cr}(\text{CO})_4\{\text{=C}(\text{OMe})\text{Ph}\}]^{2-}$ . S. Lee and N. J. Cooper